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Energy Procedia 4 (2011) 4985–4992

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GHGT-10

Storage of carbon dioxide captured in a pilot-scale biogas upgrading plant by accelerated carbonation of industrial residues

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Abstract

This work reports the preliminary evaluations obtained within the UPGAS-LOWCO₂ project (LIFE08 ENV/IT/000429) concerning innovative methods for biogas upgrading through CO₂ capture and storage. One of the methods studied in this project is chemical absorption of the CO₂ contained in landfill gas with a KOH solution followed by carbonation of the spent solution with selected industrial residues to regenerate the alkaline solution and store CO₂ in a solid phase (calcite). This paper presents the main results of the lab scale experiments carried out to evaluate the effects of the main operating parameters on the carbonation reaction so to identify the conditions that allow to maximize the CO₂ uptake of the solid residues and the percentage of KOH that can be regenerated for the absorption process. These results provide the dataset for the design of a pilot plant unit to be built and operated in the follow-up of the project.

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Keywords: biogas upgrading; CO₂ capture and storage; alkaline industrial residues; carbonation; alkali regeneration

1. Introduction

About 80% of the anthropogenic greenhouse gas (GHG) emissions generated in 2006 by EU-27 countries (5.14 Gt CO₂-equivalent) were due to the supply and use of energy (including fuel consumption from transport) [1]. Total GHG emissions in the EU have shown a decreasing trend in the last few years (7.7% reduction in 2006 compared to 1990 levels), owing to the adoption and implementation of specific policies and measures, although more efforts will be needed to meet the 20% reduction target set by the EU for the year 2020 [1]. Some countries in particular have even increased their emissions compared to the reference year; for example, a 7.4 % emission increase in 2007 compared to 1990 was reported for Italy [2]. It is worth noting that one of the sectors that showed the highest decrease in GHG emissions (31.5% reduction for EU-27 countries in 2006 compared to 1990) were waste and wastewater management activities [1].

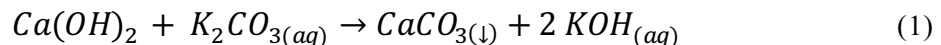
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Although waste management remains one of the main sources of anthropogenic methane emissions, contributing roughly to one fifth of global emissions, several measures, and in particular improved landfilling practices and landfill gas recovery, are showing to exert significant effects in terms of emission reductions [1]. In particular, a key EU policy towards this achievement is the Landfill Directive that has established limits regarding the maximum amount of biodegradable waste that can be landfilled and has made mandatory the installation of gas recovery facilities in all existing EU landfill sites by 2009.

The commercial recovery of CH₄ from landfill gas as a source of renewable energy has been practised at the full scale since 1975 and currently globally exceeds 105 Mt CO₂-equivalent/year [3]. Landfill gas and biogas generated from anaerobic digestion in general is mainly used for heat and power generation, however it is also being increasingly used in some EU countries, such as Switzerland and Sweden, as vehicle fuel [4]. For some applications, such as injection in the gas grid and utilization as vehicle fuel, biogas pretreatment in order to increase its CH₄ content by removing CO₂ and other components (e.g.: H₂S, O₂, dust) is required. Several methods are currently adopted for biogas upgrading such as absorption with water or chemicals, pressure swing adsorption and membrane separation. The CO₂ separated from the upgraded gas is generally emitted into the atmosphere. Since this carbon dioxide is of biogenic origin, its emissions may be regarded as climate neutral; hence, by permanently capturing and storing the separated CO₂, negative emissions may be obtained.

In the GHERL project ("GreenHouse Effect Reduction from Landfills", LIFE05 ENV/IT/000874) the feasibility of a process based on chemical absorption with an aqueous solution of potassium hydroxide (KOH) for upgrading landfill gas and capturing CO₂ was demonstrated with the construction and operation of a pilot-scale plant in a landfill site in Italy [5]. In this process, the absorption product was a liquid solution containing dissolved potassium carbonate (K₂CO₃), whereas no further CO₂ storage processes were considered. The conclusion of that study was that the competitiveness of this process with respect to other biogas upgrading and CO₂ capture techniques depended on the possibility of selling the final product (K₂CO₃) or of regenerating the KOH solution. The latter option is investigated within the ongoing UPGAS-LOWCO₂ project ("UP-grading of landfill GAS for LOWering CO₂ emissions", LIFE08 ENV/IT/000429), in which the proposed regeneration process is also aimed at storing CO₂ in a solid, thermodynamically stable and environmentally sound form. The regeneration step is based on the well known causticizing reaction that is used in the chemical recovery process of the kraft pulping method to produce precipitated calcium carbonate (PCC), e.g.: [6]; in this process, as shown in Equation 1, an alkaline carbonate, such as Na₂CO₃ or K₂CO₃, is added to a Ca(OH)₂ solution producing the corresponding hydroxide (NaOH or KOH) and precipitating calcite (CaCO₃).



Using raw calcium hydroxide for such a process would not make any sense from the CO₂ mitigation view point, since it is manufactured by calcination of limestone, releasing carbon dioxide into the atmosphere. Therefore, in order to obtain a net reduction of CO₂ emissions, in this project industrial waste residues were tested as alternative alkalinity sources. Several studies have shown the feasibility of using different types of industrial residues, characterized by a high content of calcium (hydr)oxide phases, such as bottom ash and air pollution control (APC) residues from waste incineration, steel slag, etc., to sequester CO₂ and improve the leaching behaviour of the residues, see e.g.: [7-10].

One of the final objectives of the UPGAS-LOWCO₂ project is to assess the viability of the integrated CO₂ absorption/alkali regeneration process at the pilot scale by adding a specifically designed carbonation reactor to the existing absorption column. In this paper the main results of the lab scale experimental activities carried out on different types of alkaline industrial residues to identify the conditions that allow to maximize the CO₂ uptake of the solid residues and the percentage of KOH regenerated for the absorption step are presented and discussed. These results are part of the preliminary evaluations required in the project to properly design a pilot-scale regeneration unit, to be built and operated in the follow-up of the project.

2. Materials and Methods

2.1 Materials

All the reagents used in the experiments (i.e.: Ca(OH)₂, K₂CO₃, KOH and HNO₃) were provided by Sigma-Aldrich (HPLC-grade or ACS-grade).

Ca(OH)₂ was used as reference material for carrying out preliminary carbonation experiments with the aim of evaluating the effect of the main operating parameters on KOH regeneration and calcite precipitation. An initial 12% wt. CaCO₃ content was measured in the Ca(OH)₂ reagent used in the experiments.

Three types of industrial residues were tested in the carbonation experiments: air pollution control (APC) residues from a waste incineration plant, stainless steel slag sampled at the outlet of the argon oxygen decarburization unit (AOD) and the finest size fraction ($d < 0.425$ mm) of the waste incineration bottom ash (BA) disposed of at the landfill where the absorption pilot plant is situated (Casa Rota landfill).

Detailed chemical, physical and mineralogical characterization data and an analysis of the leaching behavior of the residues tested in the carbonation experiments, as well as a description of the employed analytical methods, are reported in previous papers (APC residues [8], AOD slag [11], Casa Rota BA [12]). For the APC residues, in order to remove most of the soluble phases, chlorides in particular, contained in the ash, a washing pretreatment was applied. The pretreatment consisted in washing the APC residues for 15 minutes with distilled water at a liquid to solid (L/S) ratio of 10 l/kg. After washing, the residues were filtered under reduced pressure and dried at 105 °C.

In Table 1, the main composition of the three tested residues is summarized. As can be noted, the amount of calcium available for the carbonation reaction, obtained as the difference between the total Ca and the CaCO₃ contents of the residues, were quite similar for the first two types of residues, whereas the bottom ash presented a significantly lower available Ca content. The main mineralogical phases detected in the washed APC residues differed completely from those retrieved in the AOD slag. This latter type of material was prevalently made up by dicalcium silicate, whereas the only reactive phase with CO₂ found in the washed ash was Ca(OH)₂. The bottom ash sample presented an intermediate composition to that of the other two materials, containing both Ca hydroxide phases (i.e.: portlandite, hydrocalumite and ettringite), and Ca silicate phases (dicalcium silicate, gehlenite, etc.).

Table 1: Estimated available calcium content (% wt.) and main mineralogy of the residues examined in this study

	% available Ca	Main mineralogy
WASHED APC RESIDUES	35.6	Portlandite; Calcite
AOD SLAG	38.3	Dicalcium silicate; Calcium fluoride; Periclase; Magnetite
CASA ROTA BA (fraction with $d < 0.425$ mm)	21.9	Calcite; Hydrocalumite; Quartz; Ettringite; Portlandite; Gehlenite

2.2 Carbonation experiments

Lab scale batch carbonation experiments were carried out in a 300 ml beaker placed in a thermostatic water bath for temperature control. At the beginning of each experiment a 100 ml distilled water slurry of the residues (or of Ca(OH)₂) was poured into the reactor. During the entire duration of the experiment the suspended solution was stirred with a paddle-type impeller at a constant rate of 250 rpm and the pH and temperature of the solution were continuously measured with a Hanna Instruments benchtop pH/T meter and recorded with a data logger. After 5 minutes, 100 ml of a 2 M K₂CO₃ aqueous solution was added to the slurry of alkaline residues and from this moment on the reaction time was taken. The final resulting K₂CO₃ concentration in the slurry (1 M) would be theoretically obtained in the spent solution produced from a CO₂ absorption unit fed with a 2 M KOH solution, assuming an hypothetical 100% conversion to carbonates. Different experiment durations were tested (from 15 to 240 minutes) in order to study reaction kinetics. At the end of each experiment, the solution was quickly filtered under reduced pressure. A 100 ml filtered sample was then titrated with a 10 M HNO₃ solution in order to quantify the different species in solution based on the buffering capacity at specific pH ranges, i.e. hydroxides ($12 \leq \text{pH} \leq 14$), carbonates ($8 \leq \text{pH} \leq 11$) and bicarbonates ($5 \leq \text{pH} \leq 7$). The filtered solid sample was dried over night at 105 °C and then the calcite content of the dried samples was measured with a Dietrich–Frühling calcimeter.

The amount of residues (or of Ca(OH)₂) used in each test was selected on the basis of the percentage of available calcium estimated for each type of material (see Table 1) in order to set the molar ratio of Ca to K₂CO₃, indicated as R in this paper, at specific values, varied in the range from 0.7 to 1.9 mol Ca/mol K₂CO₃. The influence of temperature on reaction kinetics was also investigated by carrying out experiments at different temperatures (25, 40 and 55 °C). Some experiments were also performed with the initial addition of 1 M KOH solution to analyze the effect on KOH regeneration and CO₂ storage produced by an incomplete conversion of KOH to K₂CO₃ during the absorption step. Such a condition would correspond to the spent solution obtained from a 3M KOH solution assuming a quite realistic (67%) conversion of hydroxides to carbonates.

3. Results

3.1 Experiments carried out with $\text{Ca}(\text{OH})_2$ as a reference material

Figure 1 shows the titration curves of the filtered solutions resulting from carbonation experiments carried out on $\text{Ca}(\text{OH})_2$ at 25 °C for different experiment durations and for two specific R values among the tested ones: 1 (see Figure 1a) and 1.2 mol Ca/mol K_2CO_3 (see Figure 1b). For both of the tested R values, a significant KOH regeneration was achieved after 1 hour of reaction; however, only for the highest R value tested, complete conversion of the carbonate/bicarbonate phases to KOH could be observed for reaction times above 1 hour, see Figure 1b. Furthermore, the R value of 1.2 mol Ca/mol K_2CO_3 exhibited an enhancing effect on reaction kinetics, doubling the amount of regenerated KOH at short reaction times (i.e. 15 minutes) compared to the one obtained for R equal to 1 mol Ca/mol K_2CO_3 . Concerning the effects of the R value on the CO_2 uptake of the residues, shown in Figure 2, as expected, the highest uptakes (520 g CO_2 /kg residues, corresponding to a complete conversion of the available Ca to CaCO_3) were measured for the lowest R value tested (0.9 mol Ca/mol K_2CO_3). An increase in the amount of $\text{Ca}(\text{OH})_2$ added to the solution above the stoichiometric value ($R > 1$ mol Ca/mol K_2CO_3) resulted in a decrease of the CO_2 uptake of the material.

These results evidenced that no R value can allow to maximize both the amount of KOH regenerated in the solution and the CO_2 uptake of the solid phase. In view of the integration of this process with the CO_2 absorption step, it was decided to operate the next experiments with alkaline industrial residues using R values above the stoichiometric ones, so to maximize the KOH regeneration yield and hence to minimize the amount of KOH make up eventually required at the inlet of the absorption unit.

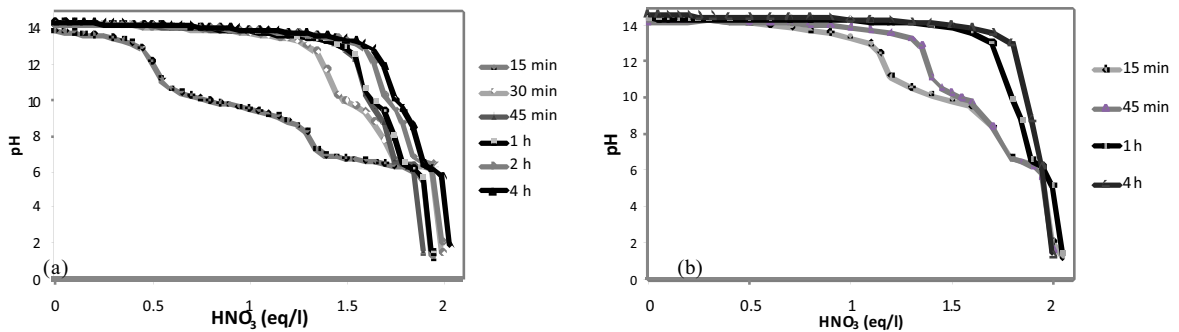


Figure 1: Titration curves of the carbonated solution obtained with $\text{Ca}(\text{OH})_2$ at 25 °C at different reaction times and R values: (a) 1; (b) 1.2 mol Ca/mol K_2CO_3

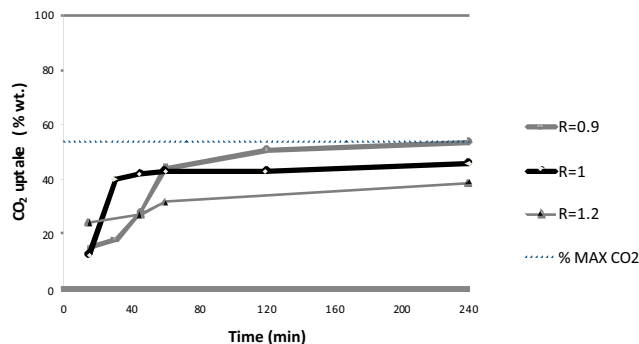


Figure 2: CO_2 uptake kinetics of the carbonated $\text{Ca}(\text{OH})_2$ at 25 °C as a function of the Ca to K_2CO_3 molar ratio

3.2 Experiments carried out with alkaline industrial residues

In Figure 3, the titration curves of carbonated solutions obtained adding different types of industrial residues with the R value that showed the highest KOH regeneration yields for $\text{Ca}(\text{OH})_2$ (1.2 mol Ca/mol K_2CO_3) are exhibited and compared to the results obtained for the reference material. For these experiments, the reaction time was of 2 hours and the operating temperature was set at 55 °C, which as will be described here below, was the investigated temperature that resulted in the best results both in terms of KOH regeneration and of CO_2 storage.

As can be noted, for the APC residues, a significantly higher concentration of KOH was retrieved in the filtered solution than for AOD slag or the tested bottom ash. This result was due mainly to the different mineralogical composition of the three types of tested residues. The washed APC residues, as previously mentioned, in fact were characterized by a rather high $\text{Ca}(\text{OH})_2$ concentration, whereas, the AOD residues and Casa Rota bottom ash were mainly made up by calcium silicates which do not provide enough alkalinity in the solution to react with potassium carbonate and hence allow to regenerate a much lower amount of KOH. Casa Rota BA actually showed a higher amount of regenerated KOH compared to AOD slag, and this was correlated to the presence of Ca hydroxide phases (portlandite and hydrocalumite) in this type of slag. Also the CO_2 uptake of the residues measured by calcimetry analysis divided by the initial available Ca content of each material, denominated CO_2 uptake efficiency, was significantly higher for the APC residues compared in particular to that of the AOD slag, see Figure 3. Hence, washed APC residues were selected as the type of industrial residues to be used in the pilot-scale carbonation reactor for KOH regeneration and CO_2 storage to be built and operated in a next step of the already cited LIFE+ project.

For these residues, a series of batch experiments aimed at selecting the operating conditions needed to maximize KOH regeneration were performed. In order to enhance the completion of the carbonation reaction, the effect of increasing reaction temperature was examined, since calcite precipitation kinetics is known to increase with temperature. As shown in Figure 4, temperature showed to exert a noteworthy enhancing effect on the amount of KOH regenerated in the carbonated solution. A temperature raise from 25 to 55 °C resulted in a KOH regeneration increase from 1.35 to 1.85 eq/l KOH, corresponding to over 90% KOH recovery for experiment durations of 1 hour. The effect exerted by the presence of an initial concentration of KOH in the K_2CO_3 ash slurry in terms of the total amount of KOH obtained in the carbonated solution is reported in Figure 5. As previously mentioned, the aim of these experiments was to assess if the presence of unconverted KOH in the spent solution from the CO_2 absorption process could hinder the carbonation reaction. Several studies (e.g.: [6]) have in fact shown that the presence of an alkaline hydroxide phase such as KOH reduces the solubility of $\text{Ca}(\text{OH})_2$ and hence the Ca supersaturation required for the precipitation of calcite. Analyzing Figure 5, it may be noted that the net amount of KOH regenerated in the carbonated solution with an initial addition of KOH (1 M) was lower than that obtained with K_2CO_3 only (1.45 compared to 1.85 eq/l KOH). The hindering effect caused by the initial presence of KOH was even more evident on the CO_2 uptake of the ash that, as can be noted in Figure 6b, resulted about 30% lower than the values measured without initial KOH addition.

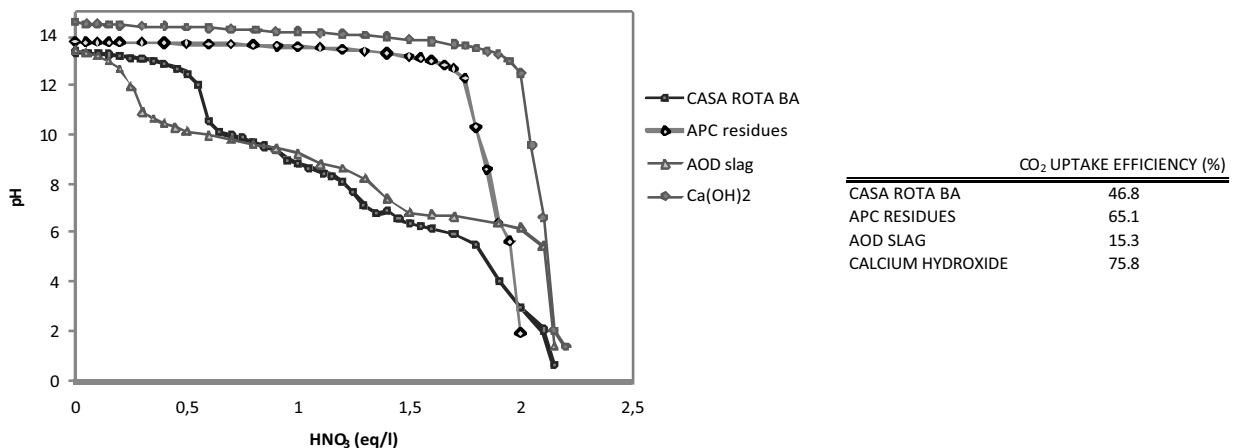


Figure 3: Comparison between the titration curves and CO_2 uptake efficiencies of the carbonated solutions obtained using $\text{Ca}(\text{OH})_2$ and the three different types of tested industrial residues ($R=1.2$ mol Ca/mol K_2CO_3 , time=2 h, $T=55$ °C)

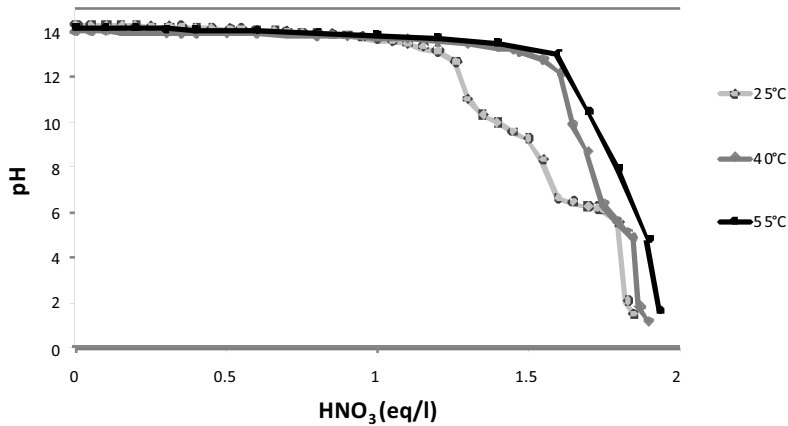


Figure 4: Influence of reaction temperature on the titration curves of the carbonated solution (washed APC residues, $R=1.2 \text{ mol Ca/mol K}_2\text{CO}_3$, time=1 h)

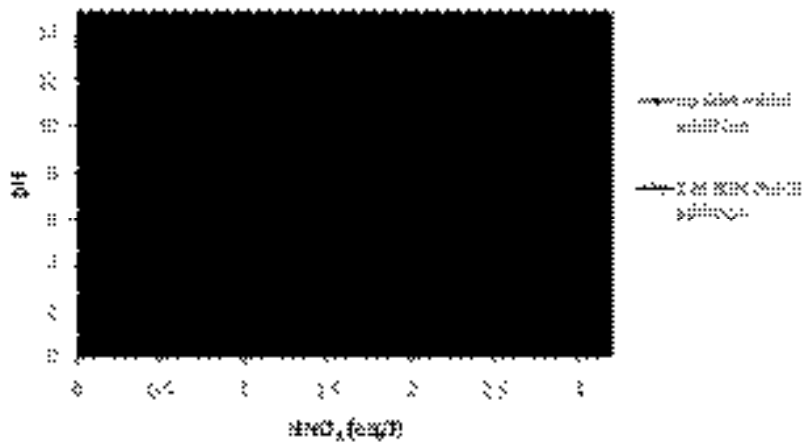


Figure 5: Comparison between the titration curves obtained for the carbonated solution (washed APC residues, $R=1.2 \text{ mol Ca/mol K}_2\text{CO}_3$, time=1 h, $T=55 \text{ }^\circ\text{C}$) with and without an initial addition of KOH

Summarizing the main results obtained by the lab scale experiments carried out on APC residues to define the preliminary design of the carbonation reactor, the operating conditions that allowed to maximize the regeneration of KOH for the absorption step and to store significant amounts of CO₂ in the solid residues are reported in Table 2. The adoption of the washing pretreatment of the ash to remove soluble salts, as well as the selection of an R value higher than 1 mol Ca/mol K₂CO₃, proved necessary in order to maximize KOH regeneration in the carbonated solution. Additionally, increasing the reaction temperature to 55 °C resulted significant in order to enhance the reaction kinetics, which achieved completion, as shown in Figure 6, after a reaction time of 30 minutes. Under these conditions, assuming a 100% conversion of KOH to K₂CO₃ in the absorption unit, a 75% efficiency of the carbonation reaction in terms of KOH regeneration was achieved (see Figure 6a). This value accounts also for the liquid losses that resulted from the filtration of the carbonated solution. As for the available calcium to calcite conversion yields found for the solid phase, a CO₂ uptake efficiency of about 65% was obtained, see Figure 6b. As previously discussed, under more realistic conditions, the presence of KOH in the spent solution from the absorption is expected; hence the results obtained under the selected operating conditions with an initial addition of KOH (1M) are also reported in Figure 6. In this case, a KOH regeneration efficiency value of about 65% was obtained, whereas the CO₂ uptake efficiency of the residues resulted just below 50%.

Table 2: Operating conditions selected for the carbonation reaction with APC residues.

PRE-TREATMENT CONDITIONS		
TYPE	Washing	
L/S	10	l/kg
TIME	15	minutes
PRECIPITATION CONDITIONS		
K ₂ CO ₃	1	mol/l
Ca	1.2	mol/l
TEMPERATURE	55	°C
TIME	60	minutes

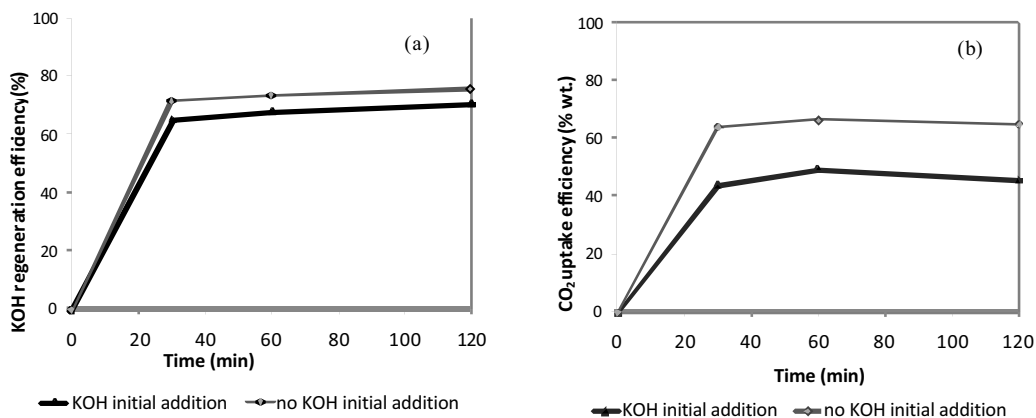


Figure 6: Results of carbonation experiments (washed APC residues, $R=1.2$ mol Ca/mol K₂CO₃, $T=55$ °C) with and without initial addition of KOH in terms of: (a) KOH regeneration efficiency and (b) CO₂ uptake efficiency of APC residues (% wt.).

The above discussed results allowed to define the operating conditions of the proposed CO₂ absorption/alkali regeneration process using APC residues, whose preliminary layout is reported in Figure 7. The spent solution is conveyed from the outlet of the absorption unit to the carbonation reactor, where it is mixed with a stream of APC residues previously treated in a washing unit to remove soluble salts, in particular chlorides. The washed residues readily dissolve in the carbonation reactor, releasing calcium hydroxide which reacts with the potassium carbonate contained in the spent solution, leading to the regeneration of the KOH required for CO₂ absorption. As shown in the experimental section, the regeneration of K₂CO₃ to KOH is not complete, due to a limited yield of the chemical reaction and to the loss of solution with the wet solid. Hence, a partial make-up of KOH is necessary to obtain the required KOH concentration at the inlet of the absorption unit. The regeneration unit allows for a maximum 75% KOH regeneration, depending on the presence or not of unreacted KOH. This obviously leads to a significant reduction of KOH consumption with respect to the absorption process without KOH regeneration. Namely, per each mol of captured CO₂, the required KOH make-up is reduced from 2 to 0.5 mol. Since it can be roughly estimated that the production of 1 mol KOH leads to the indirect release of 1.6 mol CO₂, related to the electricity required in the chlor-alkali process, this means that the proposed alkali absorption/regeneration process for biogas upgrading becomes globally slightly carbon negative, since around 0.8 mol CO₂ are emitted for the manufacturing of the KOH make-up required per 1 mol CO₂ captured and stored as carbonates. An improvement of this figure can be expected through the optimization of the solid-liquid separation step, the improvement of the APC residues washing step or by using other residues rich in free lime but characterized by a lower chlorides content.

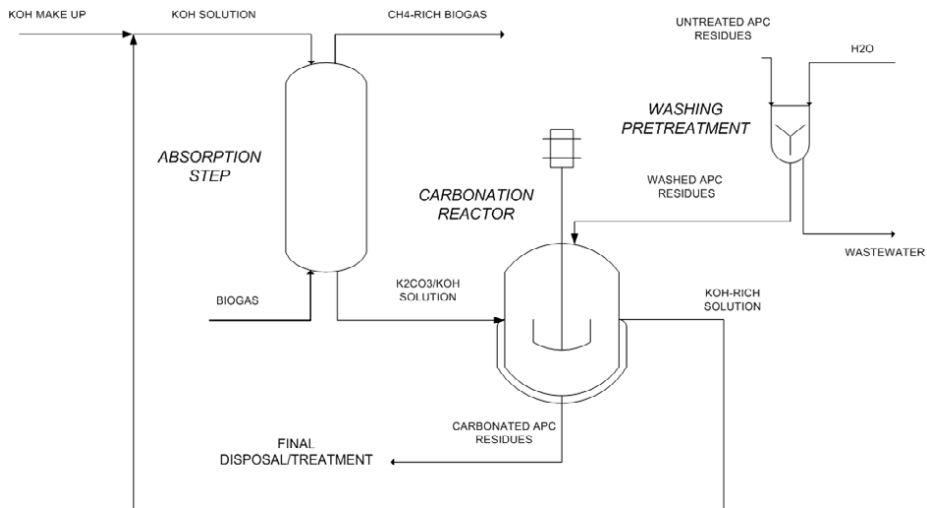


Figure 7: Preliminary layout of the proposed integrated CO₂ absorption/alkali regeneration process using APC residues

4. Conclusions

The results of the lab scale activities carried out within the first phase of the UPGAS-LOWCO₂ project showed the feasibility of using alkaline industrial residues to regenerate the outlet solution of an alkali absorption column for landfill gas upgrading while permanently storing the captured CO₂. The residues that showed the highest KOH regeneration capacity, due to their chemical, physical and mineralogical composition were the washed APC residues. Preliminary results indicated that, applying the selected operating conditions, around 65-70% of the KOH solution could be regenerated for the absorption step, while about 200 g CO₂/kg washed APC residues could be permanently stored as calcite. Before the final design of the pilot scale carbonation reactor, lab scale experiments will be carried out also on real samples of the solution produced by the existing pilot scale absorption column in order to confirm these data.

Acknowledgements

The authors would like to acknowledge the financial support of the European Commission through the Life+ Environment Policy and Governance program.

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